Metal–Organic Frameworks

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Dynamic Motion of Building Blocks in Porous Coordination Polymers**

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The design and construction of metal–organic crystal architectures have been widely studied, and a variety of frameworks have been prepared through self-assembly processes.[1] In particular, porous coordination polymers (PCPs) are currently receiving considerable attention in view of their possible functions in sorption, separation, and guest alignment.[2]

The characteristics of the increasing number of PCPs have been extensively studied. Crystal structures of PCPs with and without guests, and thermodynamic sorption isotherms are typical research topics; however, these topics investigate static aspects of the frameworks. The unique advantages of PCPs are their increased flexibility and dynamics compared to inorganic porous materials.[3] The nature of the flexibility depends strongly on the characteristics of the organic ligands used to build the frameworks. When the ligands contain mobile parts (for example, groups that undergo rotation or libration), dynamic motion may occur inside the frameworks in the solid state, even at room temperature.

Molecular motion in crystalline solids has received much attention, and various solids containing mobile groups have been designed and synthesized.[4] Compounds that are capable of rotational motion in response to outside driving forces such as light, heat, or electric fields are intriguing for the development of nanoscale devices. Studies of such solids have mainly focused on the construction of discrete molecular

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compounds; however, extended networks containing not only a mobile component, but also a rigid framework that maintains the integrity of the lattice are considered to be ideal structures for nanoscale applications.[5] From this point of view, we have investigated PCPs as a basis for creating crystalline polymer networks with responsive rotational groups. The large void space and easily modified designs of PCPs make these materials suitable for this purpose. Herein, we synthesize PCPs containing rotational organic parts and characterize their dynamic behavior with solid-state ^{2}H NMR spectroscopy, sorption measurements, and differential scanning calorimetry (DSC). In addition, we regulate their dynamic motion by guest sorption.

A pillared layer structure is a useful topology for the construction and modification of porous frameworks.[6] We first explored the solid-state dynamics of such a compound, in which the layers consist of Cd^{2+} and 2-sulfoterephthalate (2-stp) ions, and the pillars are pyrazine (pyz) molecules.[7] $\{[CdNa(2\text{-stp})(pyz)_{0.5}(H_2O)](H_2O)\}_n$ (**1**$\supset H_2O$) was synthesized by the reaction of $Cd(NO_3)_2{\cdot}4H_2O$ with 2-sulfoterephthalate, NaOH, and pyrazine in water/ethanol. Figure 1a shows the structure of **1**$\supset H_2O$ determined by single-crystal X-ray diffraction at 223 K. The neutral layers consisting of Cd^{2+}, Na^+, and 2-sulfoterephthalate ions are parallel to the *ac* plane, and the pyrazine ligands connect the layers to form the 3D pillared layer structure. The structure of **1**$\supset H_2O$ contains channels (filled by water molecules) with dimensions of 5×5 Å^2 that run along the *a* direction. The distance between the nitrogen atoms of adjacent pyrazine ligands along the *a* direction is 7.04 Å.

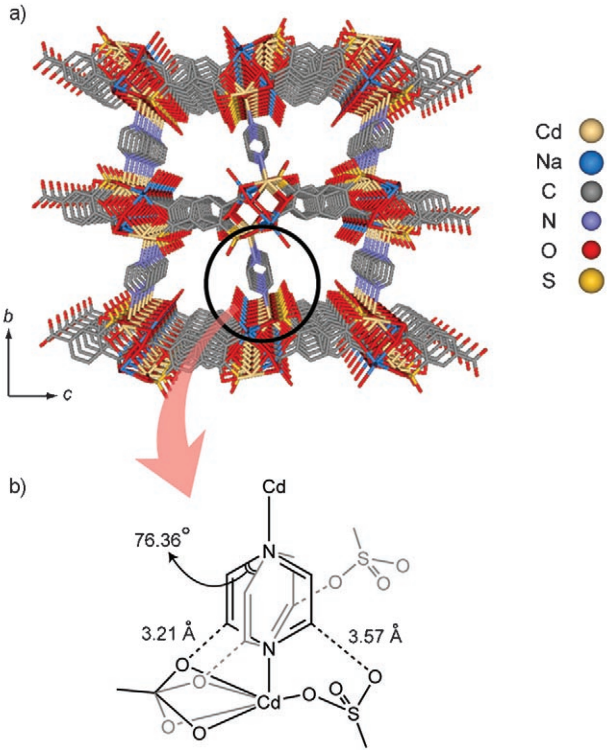

Figure 1. Crystal structure of **1**$\supset H_2O$ at 223 K. a) The pillared layer structure viewed down the *a* direction. Hydrogen atoms and guest water molecules are omitted. b) Illustration of the disorder of a pyrazine molecule (circled in (a)) and a 2-sulfoterephthalate ion around a Cd^{2+} center. Dashed lines indicate C−H⋯O interactions.

The pyrazine molecule and the 2-sulfoterephthalate ion are disordered over two conformations, each with an occupancy of 0.5 (Figure 1b). In each conformation, two C−H⋯O interactions[8,9] occur between the pyrazine ring and oxygen atoms from one carboxylate group (3.21 Å) and the sufonate group (3.57 Å) of the 2-sulfoterephthalate ion. The dihedral angle between the planes of the pyrazine rings in the two conformations is 76.36°. Thus, the pyrazine pillars are isolated enough from the rest of the framework to rotate about their N–N axes.

For solid-state ^{2}H NMR spectroscopy experiments, partially deuterated **1**$\supset H_2O$, $\{[CdNa(2\text{-stp})([D_4]pyz)_{0.5}(H_2O)](H_2O)\}_n$ (**1d**$\supset H_2O$) was synthesized by using [D$_4$]pyrazine in the procedure described above. The powder X-ray diffraction (XRD) patterns of **1**$\supset H_2O$ and **1d**$\supset H_2O$ both match the powder XRD pattern simulated from the single-crystal structure of **1**$\supset H_2O$ (see Supporting Information). This result demonstrates that the topology of the framework in **1d**$\supset H_2O$ is identical to that in **1**$\supset H_2O$.

To study the dynamics of the empty framework, we dried **1d**$\supset H_2O$ under reduced pressure at 323 K for 12 h to remove guest water molecules. The ^{2}H NMR spectra of anhydrous **1d** recorded at 193–293 K are displayed in Figure 2a. The line shape changes significantly with temperature. At 293 K, a splitting of 21 kHz is observed. At 193 K, the experimental spectrum is axially symmetric, with a splitting of 123 kHz between opposite edges, which agrees with the quadrupole coupling constant observed for a pyrazine ring in a rigid lattice.[10] To explain the changes in line shape, spectral simulations were carried out by describing the motion of the pyrazine ring as a four-site jump between orientations at angles of 0, 76.4, 180, and 256.4° about the N–N axis (chosen based on the disordered structure of **1**$\supset H_2O$) at a single jump frequency (Figure 2c). The population of each site was defined as 0.25. The simulated spectra (Figure 2b) are in good agreement with the observed spectra over the temperature range studied, confirming the validity of this rotation model. The ring undergoes jumps at a rate of 2.0×10^4 s^{-1} at 193 K and at a rate of 1.0×10^5 s^{-1} at 293 K. A pre-exponential factor of 2.4×10^6 s^{-1} and an activation energy of 7.7 kJ mol^{-1} for the four-site jump motion were determined from an Arrhenius plot (see Supporting Information). The activation energy is quite small and is nearly identical to the C−H⋯O bond energy reported previously.[9,11]

We also analyzed the dynamics of as-synthesized **1d**$\supset H_2O$, in which the pores are filled with guest water molecules. The mobility is identical that of anhydrous **1d** over the same temperature range. This result suggests that the potential barrier for rotation of the pyrazine pillars in **1d** is too small for guest sorption to interrupt the rotation.

Therefore, to make a guest-responsive dynamic framework, we prepared a PCP containing bulkier rotational groups, $[Zn_2(1,4\text{-ndc})_2(dabco)]_n$ (**2**; 1,4-ndc = 1,4-naphthalenedicarboxylate, dabco = 1,4-diazabicyclo[2,2,2]octane).[12] In this framework, paddle-wheel Zn^{2+} dimers are linked by 1,4-naphthalenedicarboxylate ions, resulting in regular square-grid-type layers parallel to the *ab* plane, and these layers are

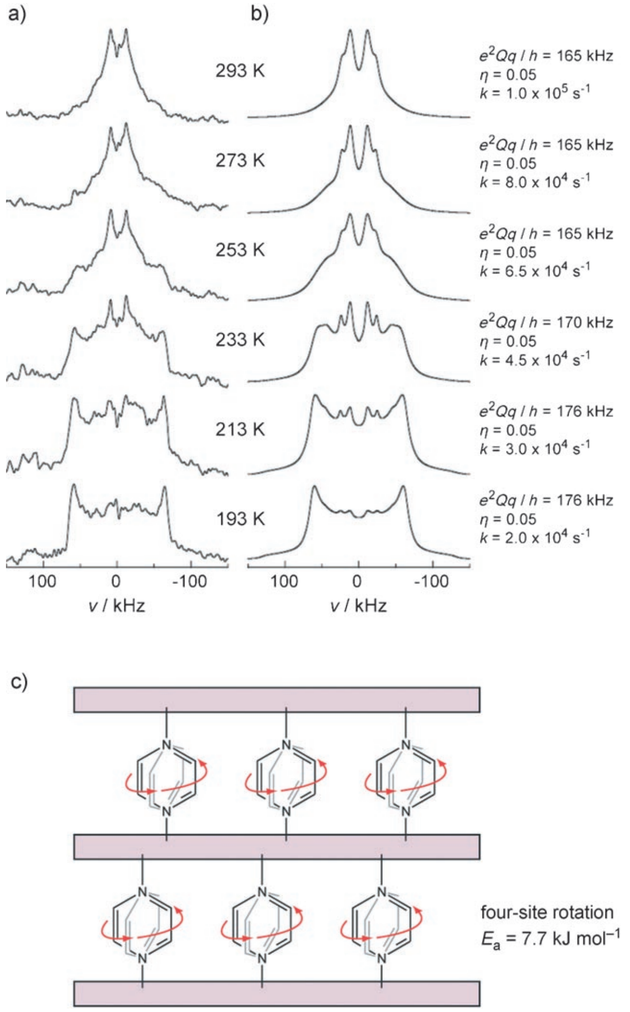

Figure 2. a) Experimental and b) simulated ^{2}H NMR spectra of **1d** at 193–293 K. The jump rates of the pyrazine rings (k), and the nuclear quadrupole coupling constants (e^2Qq/h) and asymmetry parameters (η) are indicated. c) Illustration of the four-site rotation of the pyrazine rings in **1**. The activation energy (E_a) is indicated.

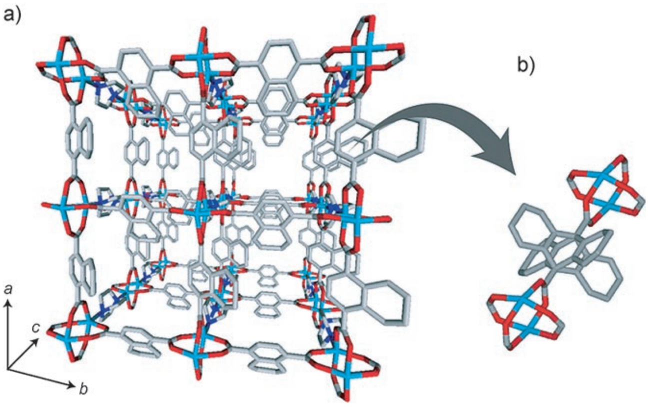

Figure 3. Crystal structure of **2** at 296 K.[12] a) The pillared layer structure viewed down the c direction. b) Four-site disorder of the naphthalene ring. Hydrogen atoms are omitted; Zn blue, C gray, O red, N dark blue.

pillared by 1,4-diazabicyclo[2,2,2]octane molecules (Figure 3a). Rectangular channels of 5.7×5.7 Å^2 run along the c direction. At 296 K, the naphthalene ring of the dicarboxylate ion is disordered over four positions (Figure 3b). Even though the naphthalene ring in **2** is larger than the pyrazine ring in **1**, there is enough void space in the framework of **2** for rotation about the C1–C4 axis of the naphthalene ring.

We synthesized partially deuterated **2** (**2d**) by using [D$_6$]1,4-naphthalenedicarboxylate and confirmed that the topology of the framework is identical to that of **2** by XRD (see Supporting Information). The ^{2}H NMR spectra for anhydrous **2d** at 193–293 K each consist of a superposition of three Pake doublets with different quadrupole coupling constants (see Supporting Information), which arise from the three types of deuterium atoms of the naphthalene ring. The spectra are temperature-dependent below 223 K, and we carried out simulations for the spectra recorded at 203–223 K. In these simulations, we modeled the motion of the naphthalene rings as a four-site flip between orientations at angles of 0, 70, 180, and 250° about the C1–C4 axis (based on the disordered structure of **2**). Rotation rates ranging from 3.0×10^6 s^{-1} at 203 K to 5×10^7 s^{-1} at 223 K were determined from the fitting. Although the mode of motion in **2** is the same as that in **1**, the activation energy of 53 kJ mol^{-1} of **2**, determined from an Arrhenius plot, is approximately six times larger than that of **1**, because of differences in packing and in the size of the mobile group.

The sorption isotherm for benzene on **2** was measured at 298 K (see Supporting Information). The isotherm displays a Type I profile, indicative of a typical physisorption process for a microporous compound. The maximum amount of benzene adsorbed is only 3 molecules per pore (100 mL g^{-1}). Considering the van der Waals volume of the benzene molecule (ca. 89 Å^3),[13] the volume occupied by the benzene molecules in the pore is $3 \times 89 = 267$ Å^3. However, the total volume of the potential solvent area in the disordered structure of **2** is 195 Å^3 per pore, as calculated using the PLATON program.[14] This value is smaller than the volume of 3 benzene molecules, suggesting that the molecules are densely adsorbed inside the pores. Thus, the benzene molecules could interfere with the free rotation of the naphthalene rings about their C1–C4 axes. The ^{2}H NMR spectra of **2d** after benzene adsorption (**2d**$\supset$C$_6$H$_6$) recorded at 193–293 K (see Supporting Information) are drastically different from those of anhydrous **2d**. Over the whole temperature range, peaks with a frequency separation of 126 kHz are observed. The associated rate of less than 10^3 s^{-1} corresponds to the slow-exchange or static limit. Thus, the rotational motion of **2d**$\supset$C$_6$H$_6$ is immediately decelerated by guest adsorption. After desorption of the benzene molecules, the four-site rotation of the naphthalene rings in **2d** restarts. Therefore, the rotational behavior is reversible by guest adsorption/desorption (Figure 4a).

Thermogravimetric analysis (TGA) of **2**$\supset$C$_6$H$_6$ shows a gradual weight loss corresponding to the loss of nearly 3 benzene molecules per pore (observed 24.1%, calculated 25.9%) over 25–150 °C, without any clear steps (see Supporting Information). However, in the heating cycle of the DSC curve of **2**$\supset$C$_6$H$_6$ over 25–150 °C, a sharp endothermic transition with an enthalpy of 4.32 kJ mol^{-1} is observed at

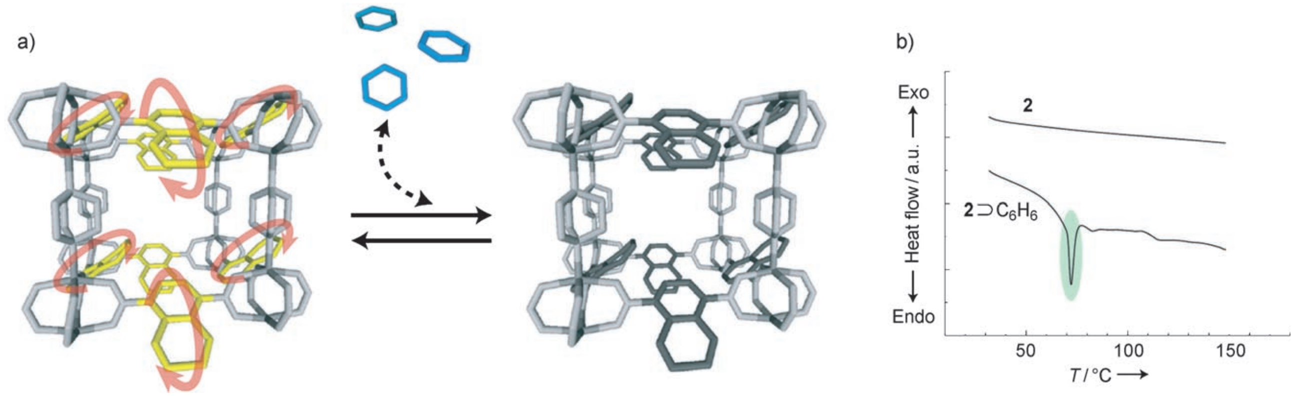

Figure 4. a) Illustration of the guest-induced reversible rotation in **2**. Benzene guests are blue; rotationally free naphthalene rings are yellow. b) DSC curves for **2** and $\mathbf{2}\supset C_6H_6$ (scan rate of 5 K min^{-1}). The endothermic peak corresponding to the transition between the static and dynamic states of $\mathbf{2}\supset C_6H_6$ is highlighted.

72 °C, in addition to the broad endothermic peak corresponding to the gradual desorption of benzene molecules (Figure 4b). The DSC profile of guest-free **2** shows no obvious peaks over the same temperature range. The difference between the profiles of $\mathbf{2}\supset C_6H_6$ and **2** indicates that an abrupt change in network dynamics accompanies guest desorption. The enthalpy associated with the peak in the DSC curve of $\mathbf{2}\supset C_6H_6$ corresponds to the enthalpy difference between the equilibrium static and dynamic states of the framework. Similar behavior was observed when acetone was used as a guest.

In conclusion, we have synthesized PCPs with rotational groups and have characterized their dynamic behavior by ^{2}H NMR spectroscopy and DSC. The designable open frameworks of PCPs can provide an organized arrangement of rotational groups in the solid state. This approach could allow the development of new types of functional crystalline solids with mobile groups for electro-optic or dielectric applications.

Experimental Section

$\mathbf{1}\supset H_2O$. $Cd(NO_3)_2{\cdot}4H_2O$ (1.11 g, 3.6 mmol) in ethanol (60 mL) was slowly added to a water/ethanol (1:1) solution (120 mL) containing 2-sulfoterephthalate (0.97 g, 3.6 mmol), pyrazine (0.40 g, 3.6 mmol), and NaOH (0.29 g, 7.2 mmol). The white microcrystals obtained were collected by filtration, washed with ethanol, and dried under reduced pressure for 1 h. Elemental analysis (%) calcd for $C_{10}H_{11}NO_{10}NaSCd$: C 25.41, H 2.35, N 2.96; found: C 25.55, H 2.69, N 2.91.

Physical measurements: Powder XRD patterns were collected on a Rigaku RINT 2000 (Ultima) diffractometer using $Cu_{K\alpha}$ radiation. TGA was carried out in a nitrogen atmosphere with a Rigaku ThermoPlus TG 8120 instrument. Elemental analysis was performed with a Thermo Finnigan EA1112 instrument. DSC was performed with a Mettler DSC822e calorimeter. The sorption isotherm of benzene (in the gaseous state) at 298 K was measured using BELSORP18-Plus volumetric adsorption equipment (BEL Japan). Solid-state ^{2}H NMR spectra were recorded on a Varian Chemagnetics CMX-300 spectrometer operated at 45.826 MHz, by using a quadrupole pulse sequence. Simulated spectra were produced with FORTRAN programs written by us.

X-ray structure determination: XRD data for a single crystal were collected on a Rigaku Mercury CCD system with $Mo_{K\alpha}$ radiation. The structure was solved by direct methods (SIR97) and refined on F^2 (SHELXL-97). Non-hydrogen atoms, except for disordered coordinated water molecules and guest molecules, were refined anisotropically. All hydrogen atoms were placed geometrically and refined with a riding model (with U_{iso} constrained to be 1.2 times U_{eq} of the carrier atom). Crystal data for $\mathbf{1}\supset H_2O$: $C_{10}H_3NO_{10}SCdNa$, $M_r = 464.58$, $0.20 \times 0.05 \times 0.05$ mm^3, orthorhombic, $Cmca$, $a = 7.038(5)$, $b = 23.12(3)$ Å, $c = 20.675(12)$ Å, $V = 3363(6)$ Å^3, $Z = 8$, $\rho_{calcd} = 1.835$ g cm^{-3}, $\lambda(Mo_{K\alpha}) = 0.71070$ Å, $T = 223$ K, $2\theta_{max} = 50.0°$, 15089 reflections collected, 1622 unique ($R_{int} = 0.0401$), 147 parameters, $R = 0.0646$ ($I > 2\sigma(I)$), $R_w = 0.1886$ ($I > 2\sigma(I)$), GOF = 1.232. CCDC-615500 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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